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805 Third Avenue
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File No.: 2954/0H643

Date: September 28, 2000

In Re Application of:

Martin TOPSOE, Asa WENDSJO, Steen YDE-ANDERSEN

Serial No: To be assigned
(U.S. National Phase of
International Application No. PCT/EP99/02102
Filed March 29, 1999
Filed: Concurrently herewith
For: METHOD OF MAKING POLYMER ELECTROLYTE
ELECTROCHEMICAL CELLS

AFFIRMATION OF PRIORITY CLAIM

Hon. Commissioner of
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Box PCT
Washington, DC 20231
Attn: DO/EO/US

Sir:

Priority has been claimed on the basis of Great Britain Patent Application No. 9806831.5 filed March 30, 1998. A certified copy of Great Britain Patent Application No. 9806831.5 was received by the International Bureau on May 25, 1999, during the pendency of International Application No. PCT/EP99/02102. Applicants herewith affirm the priority claim of the aforesaid Great Britain patent application.

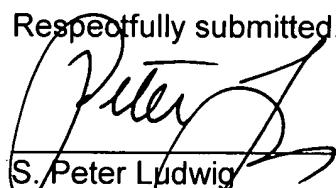
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425 RUE DE PONT 29 SEP 2000

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Page 2

Dated: September 28, 2000

Respectfully submitted,


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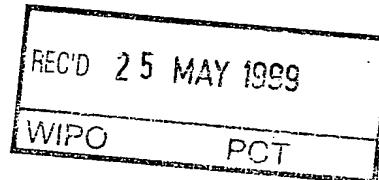
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Dated 8 April 1999

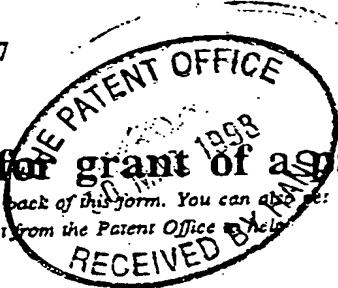
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Patents Act 1977
(Schedule 16)The
Patent
OfficeJIMAR98 E349717-1 C13295
P01/7700 25.00 - 9806831.5

The Patent Office

Cardiff Road
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Request for grant of a patent

(See the notes on the back of this form. You can also get:
an explanatory leaflet from the Patent Office which you fill in this form)

1. Your reference

JIM/LJ/PO2055

2. Patent application number

(The Patent Office will fill in this part)

30 MAR 1998

9806831.5

3. Full name, address and postcode of the or of
each applicant (underline all surnames)DANIONICS A/S
HESTEHAVEN 21J
DK-5260 ODENSE S
DENMARK

Patents ADP number (if you know it)

If the applicant is a corporate body, give the
country/state of its incorporation

DENMARK

C7485167C21

4. Title of the invention

POLYMER ELECTROLYTE ELECTROCHEMICAL CELL

5. Name of your agent (if you have one)

ELKINGTON AND FIFE

"Address for service" in the United Kingdom
to which all correspondence should be sent
(including the postcode)ELKINGTON AND FIFE
PROSPECT HOUSE
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SEVENOAKS
KENT
TN13 1XR

Patents ADP number (if you know it)

67004

6. If you are declaring priority from one or more
earlier patent applications, give the country
and the date of filing of the or each of these
earlier applications and (if you know it) the or
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Country

Priority application number
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(day/month/year)7. If this application is divided or otherwise
derived from an earlier UK application,
give the number and the filing date of
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Number of earlier application

Date of Filing
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Patents Form 1/77

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? Answer "Yes" if:
- any applicant named in part 3 is not an inventor, or
 - there is an inventor who is not named as an applicant, or
 - any named applicant is a corporate body.

YES

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Continuation sheets of this form:	NONE
Description	14
Claim(s)	6
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Translations of priority documents	-
Statement of inventorship and right to grant of a patent (Patents Form 7/77)	4
Request for preliminary examination and search (Patents Form 9/77)	-
Request for substantive examination (Patents Form 10/77)	-
Any other documents (please specify)	-

11. I/We request the grant of a patent on the basis of this application.

Signature

Date

30/03/1998

12. Name and daytime telephone number of person to contact in the United Kingdom

Mr J I MARCHANT
01732 458881

Polymer Electrolyte Electrochemical C 11

5 The recent development of electrochemical cells based on lithium containing negative electrode structures has allowed the fabrication of cells of high energy density. Cells have been obtained, which display energy densities beyond 200 Wh/l and even 250 Wh/l has been reported.

10 In order to reach such high energy densities, the capacity utilisation of the active materials in the cell should be high. As further high rate capabilities of the electrochemical cells are sought, electrolyte phases should provide low impedance.

15 Traditionally, high conductivity electrolytes have been liquid electrolytes. Such electrolytes are used in lithium cells of intercalation compound electrodes; The positive electrode structures are based on transition metal oxides operating at a potential close to 4V vs. Li/Li⁺. Negative 20 electrode structures of carbons and graphites may be applied, which reversibly intercalate lithium at a potential close to the potential of metallic lithium. Such cells are referred to as lithium-ion cells, as the active lithium is always in its ionic form. Alternatively, 25 negative electrode structures of alloys such as Li-Al and Li-Sn may be used. Such cells will be referred to as lithium-alloy cells. All of the above configurations provide voltages close to 4V.

30 As high energy density and high rate capability imply reduced safety, an important objective in the development of such electrochemical cells has been to improve the safety aspects of the use of such cells.

The main improvement in terms of safety has been the substitution of carbon or alloy structures for the pure lithium metal negative electrode structures. During operation of lithium metal based negative electrodes, 5 dendrites form, which penetrate the cell separator and shorten the cell. Although the risk of dendrite formation cannot be completely ignored in lithium-ion or lithium-alloy cells, especially during high-rate charging, the risk is strongly reduced compared to lithium metal cells.

10

Another problem associated with the liquid electrolytes traditionally applied is leakage of the electrolyte. The leakage may not only lead to cell failure; penetration of the corrosive fluid may destroy the electronic device in 15 which the cell is used.

20

One approach to solve these problems has been the application of solid state electrolytes. The use of such electrolytes will merely eliminate the risk of dendrite formation and of electrolyte leakage.

25

US 5,296,318 to Bell Communication Research describes the use of a polymer electrolyte based on polyvinylidenefluoride-hexafluoropropylene copolymer, which is present in the electrolyte phase in an amount corresponding to 30-80% by weight of the electrolyte system. Electrochemical cells based on such polymer electrolyte has significantly lower conductivity than cells based on a liquid electrolyte.

30

US 5,418,091 to Bell Communication Research describes a multistep process for the application of polymer electrolytes as described in the above US 5,296,318.

The above patents mirror the problem of solid state electrolytes, and in particular of polymer electrolytes, which are the best ambient temperature candidates; their conductivity is too low. Due to the low conductivity of the 5 polymer electrolytes, the performance of the electrochemical cells in which they are applied is strongly reduced compared to liquid electrolyte cells.

Therefore, there is a strong need for polymer electrolytes 10 and process technology therefor, which will provide electrochemical cells of high performance and safety, and which can be applied by a simple, low cost process.

It is thus an objective of the present invention to provide 15 such polymer electrolytes, which display performance similar to liquid electrolytes, however, with improved safety, and processes therefor, which are simpler than traditional processing of polymer electrolytes

20 The objective is accomplished by a polymer electrolyte, which has a significantly lower polymer content than traditional polymer electrolytes, and which can be processed according to a simple temperature scheme.

25 Surprisingly it has been found, that a range of polymer electrolytes based on fluorocarbons exists, which upon heating to a certain dissolution temperature T_{dissol} produce low viscosity solutions. Such solutions are stable between room temperature and the above T_{dissol} . When additionally 30 heated to a gelling temperature T_{gel} , $T_{gel} > T_{dissol}$, they undergo a transition, in that they upon cooling form gels of significantly higher viscosity than for the above solutions.

As used herein, a gel is defined as a system of which the modulus of elasticity is higher than the modulus of loss, i.e. it has dominating elastic properties over viscous properties

5

Such processing scheme is applied to polymer electrolytes of a polymer content in the range of 1-12% by weight of the electrolyte system. The electrolytes are then easily processable in that they are treated as liquid electrolytes 10 until the final process step, during which the gelling takes place.

Thus, according to the present invention an electrolyte precursor comprising one or more solvents, one or more salts and a polymer processing the above features is heated to a temperature sufficient for the dissolution of the polymer in the solvent(s). The temperature, T_{dissol} , however, should not exceed the temperature, at which gelling of the polymer takes place upon subsequent cooling. 15 Subsequently, the electrolyte precursor solution is incorporated into the electrochemical cell at a temperature in the range from room temperature to T_{dissol} . Following incorporation, the electrochemical cell is heated to a temperature T_{sel} . Upon subsequent cooling from T_{sel} to room 20 temperature, a significant gelling of the electrolyte takes 25 temperature, a significant gelling of the electrolyte takes place, and the resulting polymer electrolyte has a significantly higher viscosity than the precursor.

In a preferred embodiment of the invention the polymer is 30 a homopolymer or copolymer from the group of monomers of vinyl fluoride, vinylidenefluoride, trifluoroethylene, tetrafluoroethylene and hexafluoropropylene, preferably a copolymer of vinylidenefluoride and hexafluoropropylene,

more preferably a copolymer of vinylidenefluoride and hexafluoropropylene of a molar weight in the range 50,000-500,000, more preferably 100,000-300,000, and a weight ratio of vinylidenefluoride and hexafluoropropylene in the range 80:20 to 90:10.

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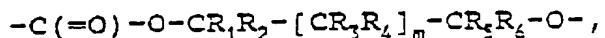
US 5,705,084 to Joseph Kejha discloses a composite solid state or semi-solid state polymer electrolyte for batteries, capacitors and other electrochemical devices, wherein the electrolyte mixture contains polyethylene oxide, polyvinylidenefluoride/hexafluoropropylene, a salt and at least one aprotic liquid. In a preferred embodiment the electrolyte comprises polyvinylidenefluoride/hexafluoropropylene in an amount in the range 0.1-70% and polyethylene oxide in an amount in the range 0.5-70% by weight of the electrolyte system, respectively. The patent discloses the coating of electrodes with solutions of the above electrolyte, prepared at 60-90°C, and the subsequent thickening of the electrolyte upon solvent evaporation. The patent, however, does not teach anything on the two stage heating and liquid phase-gel behaviour of the electrolyte, and the advantages thereof.

PCT/EP97/07275 to Danionics discloses a lithium secondary battery comprising an immobilized electrolyte containing one or more alkali metal salts, one or more non-aqueous solvents and an immobilizing polymer, wherein the immobilizing polymer is selected from the group consisting of cellulose acetates, cellulose acetate butyrates, cellulose acetate propionates, polyvinylidene fluoride-hexafluoropropylenes and polyvinylpyrrolidone-vinyl acetates with the proviso that in the case of polyvinylidene fluoride-hexafluoropropylenes, the polymer

is present in an amount of at most 12% by weight based on the weight of the salts, solvents and polymer of the electrolyte system. The patent application discloses a method for the preparation of a lithium secondary battery comprising the steps of solvent mixing, salt dissolution, addition of immobilizing polymer and sandwiching of the electrode between positive and negative electrodes. The patent, however, teaches nothing on the two stage heating scheme and the advantageous performance of the so treated electrolyte.

In a preferred embodiment of the present invention the electrolyte comprises one or more solvent(s) selected from the groups (a) to (e):

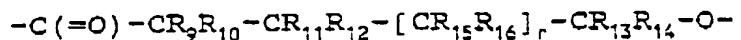
(a) alicyclic carbonates represented by the following general formula:



wherein each of R₁, R₂, R₃, R₄, R₅ and R₆ independently represents hydrogen or a C₁-C₄ alkyl group and m is 0 or 1, preferably ethylene carbonate or propylene carbonate;

(b) aliphatic carbonates represented by the general formula R₇[OC(O)]_pOR₈, wherein each of R₇ and R₈ independently represents a C₁-C₄ alkyl group, and p is an integer equal to 1 or 2, preferably dimethyl carbonate or diethyl carbonate;

(c) lactones in the form of cyclic esters represented by the general formula:



wherein each of R₉, R₁₀, R₁₁, R₁₂, R₁₃, R₁₄, R₁₅ and R₁₆ independently represents hydrogen or a C₁₋₂ alkyl group and r is 0 or 1, preferably γ -valerolactone or γ -butyrolactone;

5 (d) esters represented by the formula R₁₇[C(O)]OR₁₈[OR₁₉]_t, wherein each of R₁₇, R₁₈ and R₁₉ independently represents hydrogen or a C_{1-C₂} alkyl group, and t is 0 or an integer equal to 1 or 2, preferably an acetate, more preferably (2-methoxyethyl)-acetate or ethyl acetate;

10 (e) glymes represented by the general formula R₂₀O(R₂₁O)_nR₂₂, in which each of R₂₀ and R₂₂ independently represents a C₁₋₂ alkyl group, R₂₁ is -(CR₂₃R₂₄CR₂₅R₂₆) - wherein each of R₂₃, R₂₄, R₂₅ and R₂₆ independently represents hydrogen or a C_{1-C₄} alkyl group, and n is an integer from 2 to 6, preferably 3, R₂₀ and R₂₂ preferably being methyl groups, R₂₃, R₂₄, R₂₅ and R₂₆ preferably being hydrogen or C_{1-C₂} alkyl groups, more preferably hydrogen.

20 In a preferred embodiment of the invention the salt of the electrolyte is selected from the group of alkali metal or ammonium salts of ClO₄⁻, CF₃SO₃⁻, AsF₆⁻, PF₆⁻ or BF₄⁻, preferably LiPF₆ and LiBF₄.

25 In a preferred embodiment of the invention the electrolyte precursor comprises solvent(s), salt(s) and polymer(s) in the compositional range from 63:25:12 to 94:5:1 percent of the total weight of the electrolyte system, preferably in the compositional range from 70:20:10 to 90:8:2 percent of the total weight of the electrolyte system, more preferably in the compositional range from 75:17:8 to 88:8:4 percent of the total weight of the electrolyte system.

In a preferred embodiment of the invention the dissolution temperature is in the range 45-80°C preferably 60-80°C, more preferably 65-75°C, and the gelling temperature is in the range 75-100°C, preferably 80-90°C, with the proviso, that
5 the gelling temperature should be higher than the dissolution temperature.

In a preferred embodiment of the invention the electrochemical cell comprises any one of the above
10 electrolyte configurations. The electrolyte may be confined in a separator consisting of a porous structure made of a polymer, preferably of polyethylene, polypropylene, polycarbonate or cellulose, the separator having a woven or non-woven structure having a pore size in the range of
15 10 x 10 nm to 1 x 1 mm and a thickness of 10-100 μ m, preferably 10-25 μ m. The cell further comprises a negative electrode structure comprising one or more compounds selected from the group of graphite, coke, carbon black, aluminium, silicon or tin, and a positive electrode
20 structure comprising one or more compounds selected from the group of lithium manganese oxides, lithium cobalt oxides and lithium nickel oxides.

In a further preferred embodiment the electrodes display
25 such a porosity, which allows the diffusion of a relatively solvent-rich electrolyte phase into the pores of the electrodes, leaving a relatively polymer-rich electrolyte phase in the volume between the electrodes. Such separation of the electrolyte in a pore-phase and a bulk-phase further
30 reduces the risk of electrolyte leakage. In the case of cell puncture, the low viscosity electrolyte phase will be bound in the pores and will not leak from the cell.

Similarly, the high viscosity bulk phase will be bound between the electrodes.

In a preferred embodiment of the invention the incorporation is applied on a wound cell, i.e. the winding of the cell is done prior to electrolyte impregnation. Such cell can be efficiently impregnated with the low viscosity electrolyte obtained from the first step of the present invention. The impregnation of wound cells further allows improved control of the solvent evaporation, i.e. the solvent composition is merely unchanged during the process, even in the case of low boiling solvents such as dimethyl carbonate and diethyl carbonate.

In a further preferred embodiment of the invention the electrolyte incorporation is carried out by a simple pouring or injection process.

The invention further covers an electrochemical cell characterised by a negative electrode structure comprising one or more compounds selected from the group of graphite and coke and a positive electrode structure comprising one or more compounds selected from the group of lithium manganese oxides, lithium cobalt oxides and lithium nickel oxides, preferably lithium manganese oxide, and a gelled polymer electrolyte, 1-12% by weight, preferably 4-8% by weight, of the total weight of the electrolyte being said polymer, which is selected from the group of homopolymers and copolymers from the group of monomers of vinyl fluoride, vinylidenefluoride, trifluoroethylene, tetrafluoroethylene and hexafluoropropylene, preferably a copolymer of vinylidenefluoride and hexafluoropropylene.

Examples**Example 1:**

5 A lithium secondary battery was prepared from a negative electrode laminate of a polymer bound carbon coated onto a copper current collector, a positive electrode laminate of a polymer bound lithium manganese oxide spinel coated onto an aluminium current collector, and an electrolyte.

10 10 The carbon was R-LIBA-A (product of Timcal, Switzerland). The lithium magnesium oxide spinel was prepared by a solid state reaction at 800°C from Li_2CO_3 and MnO_2 and had a specific capacity of 120 mAh/g. In the case of both 15 electrodes, the polymeric binder was EPDM (ethylene propylene diene polymethylene).

20 The battery laminate was wound from the above negative and positive electrode laminates and a microporous polyethylene separator. The entire battery laminate was placed in plastic-coated aluminium "coffee-bag" container.

25 The electrolyte was prepared by mixing ethylene carbonate (EC) and diethyl carbonate (DEC) in a volume ratio of 2:1, adding LiBF_4 and LiPF_6 (60% to 40% by mole) to obtain a 1M solution of $\text{LiBF}_4/\text{LiPF}_6$ in EC/DEC, heating the above liquid electrolyte solution to 70°C, and adding at this temperature 5% by weight of polyvinylidene fluoride-hexafluoropropylene (PVDF/HFP) (KYNERFLEX 2822 from Elf Atochem) to the 30 solution to obtain a 5% by weight solution of PVDF/HFP in 1M $\text{LiBF}_4/\text{LiPF}_6$ in EC/DEC. The polymer electrolyte was stirred at 70°C for ten min. before cooling to room temperature.

During these last stages, in the temperature range RT-70°C, the polymer electrolyte is in its liquid state.

5 The liquid polymer electrolyte was injected into the above battery laminate at ambient temperature. Subsequently, the battery was heated to 85°C for ten minutes. The battery was allowed to cool to room temperature.

10 At this stage, the polymer electrolyte was gelled, displaying in the bulk phase between the electrodes a viscosity significantly higher than observed for the free polymer electrolyte.

15 The battery prepared had an active electrode area of 365 cm² and, subsequent to charging to 4.2V, an internal impedance of 49 mΩ at 1kHz. When cycled between 4.2V and 2.5V at 500 mA, the battery displayed an initial capacity of 358 mAh. After 400 cycles, the capacity was 299 mAh, say 84% of the initial capacity. At 1.25A discharge rate, an initial capacity of 210 mAh was observed.

20 Upon nail penetration ($\varnothing=5\text{mm}$, $F=6000\text{N}$) the battery short-circuited, however, no leakage of electrolyte was observed on the surface of the battery upon visual inspection.

25

Comparative Example 1a:

30 A battery laminate was produced and packed according to example 1. A liquid state polymer electrolyte was prepared according to example 1.

12

The liquid polymer electrolyte was injected into the above battery laminate at room temperature. Compared to example 1, the battery was not heated subsequent to the electrolyte injection.

5

The battery having the same dimensional characteristics as the battery of example 1, had an internal impedance of 42 m Ω at 1kHz. When cycled between 4.2V and 2.5V at 500 mA, the battery displayed an initial capacity of 408 mAh. 10 After 400 cycles, the capacity was 343 mAh, say 84% of the initial capacity. At 1.25A discharge rate, an initial capacity of 280 mAh was observed.

Upon nail penetration ($\varnothing=5\text{mm}$, $F=6000\text{N}$) the battery short-circuited. Leakage of electrolyte was observed on the surface of the battery upon visual inspection. 15

Comparative example 1b:

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A battery laminate was produced and packed according to example 1.

25

The electrolyte was prepared by mixing ethylene carbonate (EC) and diethyl carbonate (DEC) in a volume ratio of 2:1, adding LiBF₄ and LiPF₆ (60% to 40% by mole) to obtain a 1M solution of LiBF₄/LiPF₆ in EC/DEC, and adding at room temperature 5% by weight of polyvinylidene fluoride-hexafluoropropylene (PVDF/HFP) (KYNERFLEX 2822 from Elf Atochem) to the solution to obtain a 5% by weight solution of PVDF/HFP in 1M LiBF₄/LiPF₆ in EC/DEC. The polymer electrolyte was stirred at room temperature for 10 min. 30

during which a partial dissolution of the polymer was observed.

The polymer electrolyte was injected into the above battery laminate at ambient temperature. It was observed, that the distribution of electrolyte within the battery laminate was poorer compared to the above examples 1 and 1a, as undissolved polymer was blocking the pores. Subsequently, the battery was heated to 85°C for ten minutes. The battery was allowed to cool to room temperature. The polymer electrolyte was gelled, displaying in the bulk phase between the electrodes a viscosity significantly higher than observed for the free polymer electrolyte.

The battery having the same dimensional characteristics as the batteries of examples 1 and 1a had an internal impedance of 150 mΩ at 1kHz. When cycled between 4.2V and 2.5V at 500 mA, the battery displayed an initial capacity of 280 mAh. After 100 cycles, the capacity was 176 mAh, say 63% of the initial capacity. At 1.25A discharge rate, an initial capacity of 138 mAh was observed.

Upon nail penetration ($\varnothing=5\text{mm}$, $F=6000\text{N}$) the battery short-circuited, however, no leakage of electrolyte was observed on the surface of the battery upon visual inspection.

Comparative example 1c:

A battery laminate was produced and packed according to example 1.

The electrolyte was prepared by mixing ethylene carbonate (EC) and diethyl carbonate (DEC) in a volume ratio of 2:1, adding LiBF₄ and LiPF₆ (60% to 40% by mole) to obtain a 1M solution of LiBF₄/LiPF₆ in EC/DEC.

5

The electrolyte was injected into the above battery laminate at ambient temperature. No gelling of the electrolyte was observed.

10 The battery having the same dimensional characteristics as the battery of example 1, had an internal impedance of 38 mΩ at 1kHz. When cycled between 4.2V and 2.5V at 500 mA, the battery displayed an initial capacity of 421 mAh. After 400 cycles, the capacity was 362 mAh, say 86% of the initial capacity. At 1.25A discharge rate, an initial capacity of 360 mAh was observed.
15

Upon nail penetration ($\varnothing=5\text{mm}$, $F=6000\text{N}$) the battery short-circuited. Leakage of electrolyte was observed on the
20 surface of the battery upon visual inspection.

Claims:

1. A method for the preparation of a polymer electrolyte electrochemical cell using an electrolyte precursor, said precursor comprising one or more solvents, one or more salts and a polymer which dissolves in the solvent at a first temperature (T_{dissol}) and which is capable of forming a gel on subsequent cooling following heating to a second temperature (T_{gel}), T_{dissol} being lower than T_{gel} , which method comprises:

- (a) heating the electrolyte precursor to T_{dissol} ;
- (b) optionally cooling the electrolyte precursor;
- (c) incorporating the electrolyte precursor into the electrochemical cell;
- (d) heating the electrochemical cell to T_{gel}
- (e) cooling the polymer electrochemical cell to ambient temperature to bring about gelling of the polymer electrolyte

2. A method for the preparation of an electrochemical cell according to claim 1, in which said polymer is a homopolymer or copolymer from the group of monomers of vinyl fluoride, vinylidene fluoride, trifluoroethylene, tetrafluoroethylene and hexafluoropropylene.

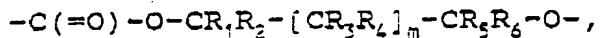
3. A method for the preparation of an electrochemical cell according to claim 2, in which said polymer is a

copolymer of vinylidenefluoride and hexafluoropropylene.

4. A method for the preparation of an electrochemical cell according to claim 3, in which said copolymer of vinylidenefluoride and hexafluoropropylene has a molar weight in the range 50.000-500.000, more preferably 100.000-300.000, and a weight ratio of vinylidenefluoride and hexafluoropropylene in the range 80:20 to 90:10.

5. A method for the preparation of an electrochemical cell according to any of the preceding claims, in which the electrolyte comprises one or more solvent(s) selected from the groups (a) to (e):

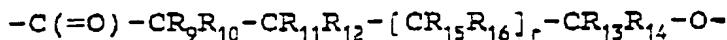
(a) alicyclic carbonates represented by the following general formula:



wherein each of R₁, R₂, R₃, R₄, R₅ and R₆ independently represents hydrogen or a C₁-C₄ alkyl group and m is 0 or 1, preferably ethylene carbonate or propylene carbonate;

(b) aliphatic carbonates represented by the general formula R₇[OC(O)]_pOR₈, wherein each of R₇ and R₈ independently represents a C₁-C₄ alkyl group, and p is an integer equal to 1 or 2, preferably dimethyl carbonate or diethyl carbonate;

(c) lactones in the form of cyclic esters represented by the general formula:



5

wherein each of R_9 , R_{10} , R_{11} , R_{12} , R_{13} , R_{14} , R_{15} and R_{16} independently represents hydrogen or a C_{1-2} alkyl group and r is 0 or 1, preferably γ -valerolactone and/or γ -butyrolactone;

10

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(d) esters represented by the formula $\text{R}_{17}[\text{C}(\text{O})]\text{OR}_{18}[\text{OR}_{19}]_t$, wherein each of R_{17} , R_{18} and R_{19} independently represents hydrogen or a C_1-C_2 alkyl group, and t is 0 or an integer equal to 1 or 2, preferably an acetate, more preferably (2-methoxyethyl)-acetate or ethyl acetate;

20

25

(e) glymes represented by the general formula $\text{R}_{20}\text{O}(\text{R}_{21}\text{O})_n\text{R}_{22}$, in which each of R_{20} and R_{22} independently represents a C_{1-2} alkyl group, R_{21} is $-(\text{CR}_{23}\text{R}_{24}\text{CR}_{25}\text{R}_{26})-$ wherein each of R_{23} , R_{24} , R_{25} and R_{26} independently represents hydrogen or a C_1-C_4 alkyl groups, and n is an integer from 2 to 6, preferably 3, R_{20} and R_{22} preferably being methyl groups, R_{23} , R_{24} , R_{25} and R_{26} preferably being hydrogen or C_1-C_2 alkyl groups, more preferably hydrogen.

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6. A method for the preparation of an electrochemical cell according to any of the preceding claims, in which the electrolyte comprises one or more salts selected from the group of alkali metal or ammonium salts of ClO_4^- , CF_3SO_3^- , AsF_6^- , PF_6^- or BF_4^- , preferably LiPF_6 and LiBF_4 .

7. A method for the preparation of an electrochemical cell according to any of the preceding claims, in which the electrolyte comprises solvent(s), salts(s) and polymer(s) in the compositional range from 63:25:12 to 94:5:1 percent of the total weight of the electrolyte system, preferably in the compositional range from 70:20:10 to 90:8:2 percent of the total weight of the electrolyte system, more preferably in the compositional range from 75:17:8 to 88:8:4 percent of the total weight of the electrolyte system.
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8. A method for the preparation of an electrochemical cell according to any of the preceding claims in which the electrolyte is confined in a separator consisting of a porous structure made of a polymer, preferably of polyethylene, polypropylene, polycarbonate or cellulose.
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9. A method for the preparation of an electrochemical cell according to claim 8, in which the separator has a woven or non-woven structure having a pore size in the range of 10 x 10 nm to 1 x 1 mm.
- 20
10. A method for the preparation of an electrochemical cell according to claim 8 or 9, in which the separator has a thickness of 10-100 μm , preferably 10-25 μm .
- 25
11. A method for the preparation of an electrochemical cell according to any of the preceding claims, in which the electrochemical cell has a negative electrode structure comprising one or more compounds selected from the group of graphite, coke, carbon black, aluminium, silicon or tin, preferably graphite,
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5 coke and carbon black, more preferably graphite, and a positive electrode structure comprising one or more compounds selected from the group of lithium manganese oxides, lithium cobalt oxides and lithium nickel oxides, preferably lithium manganese oxides, more preferably lithium manganese oxide LiMn_2O_4 of spinel structure.

- 10 12. A method for the preparation of an electrochemical cell according to any of the preceding claims, in which the dissolution temperature T_{dissol} is in the range 45-80°C, preferably 60-80°C, more preferably 65-75°C, and the gelling temperature T_{gel} is in the range 75-15 100°C, preferably 80-90°C, with the proviso, that T_{gel} should be higher than T_{dissol} .
- 20 13. A method for the preparation of an electrochemical cell according to any of the preceding claims, in which the electrochemical cell is wound prior to electrolyte impregnation.
- 25 14. A method for the preparation of an electrochemical cell according to any of the preceding claims, in which the electrolyte incorporation is carried out by pouring or injection.
- 30 15. A method for the preparation of an electrochemical cell according to any of the preceding claims, in which the electrodes of the electrochemical cell display such a porosity, that it allows for the diffusion into the pores of the electrodes of a relatively solvent-rich electrolyte phase, leaving a

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relatively polymer-rich electrolyte phase in the volume between the electrodes.

16. An electrochemical cell characterised by a negative electrode structure comprising one or more compounds selected from the group of graphite and coke and a positive electrode structure comprising one or more compounds selected from the group of lithium manganese oxides, lithium cobalt oxides and lithium nickel oxides, preferably lithium manganese oxide, and a gelled polymer electrolyte, 1-12% by weight, preferably 4-8% by weight, of the total weight of the electrolyte being said polymer, which is selected from the group of homopolymers and copolymers from the group of monomers of vinyl fluoride, vinylidene fluoride, trifluoroethylene, tetrafluoroethylene and hexafluoropropylene, preferably a copolymer of vinylidene fluoride and hexafluoropropylene.

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Abstract**Polymer Electrolyte Electrochemical Cell**

The invention relates to a method for the preparation of
5 a polymer electrolyte electrochemical cell using an
electrolyte precursor, said precursor comprising one or
more solvents, one or more salts and a polymer which
dissolves in the solvent at a first temperature (T_{dissol})
and which is capable of forming a gel on subsequent
10 cooling following heating to a second temperature (T_{gel}),
 T_{dissol} being lower than T_{gel} , which method comprises:

- (a) heating the electrolyte precursor to T_{dissol} ;
- 15 (b) optionally cooling the electrolyte precursor;
- (c) incorporating the electrolyte precursor into the
electrochemical cell;
- 20 (d) heating the electrochemical cell to T_{gel}
- (e) cooling the polymer electrochemical cell to
ambient temperature to bring about gelling of the
polymer electrolyte

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Preferably the polymer is a homopolymer or copolymer from
the group of monomers of vinyl fluoride,
vinylidenefluoride, trifluoroethylene, tetrafluoroethylene
and hexafluoropropylene.

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